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Statistical Properties of Vibrational Energy Levels in C_6H_6 *

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Abstract   The statistical properties of vibrational energy levels in C_6H_6 are analyzed. The results show that they belong to a completely different type of which the spectral rigidity is larger but the fractal dimensional function is smaller than both the Wigner law and Poisson law   and this new statistical property is called the low Poisson law. In fact this special statistical property reflects the speciality in the structure of C_6H_6 in a way.

Keywords C_6H_6 Vibrational energy levels   Statistical properties

1   Introduction

Owing to the foundation of the random matrix theory in the 1960s the basic research work about level fluctuation spectra has made a rapid progress[1-10] . Not only a series of statistical theories as well as the corresponding models of level fluctuation have been established but also the research domain has been expanded both from nucleus to atom or molecule systems and from observed spectra to eigenvalue spectra. Usually a spectrum can be separated quite generally into a smoothly varying average part and a fluctuating part describing the deviations from the average. The

statistical analysis then concentrates on the fluctuating part. It is known that the complex systems exhibit universal fluctuation properties. Two kinds of them are particularly important   a Poisson law describing the uncorrelated random level spectra   Poisson spectrum and b Wigner law which describes the Gaussian orthogonal ensemble of the random matrix spectra. The nearest neighbor spacing   NNS   distributions of them are given by

$$P s   = \begin{cases} e^{-s} & \text{Poisson} \\ \dfrac{\pi}{2}s \exp\left(-\dfrac{\pi s^2}{4} \right) & \text{Wigner} \end{cases} \qquad 1$$

$P s$ is the probability to find a level with the interval

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spacing between its nearest neighboring levels s. Both the Poisson distribution and the Wigner one can be derived from a simple probability argument which results in an integral equation for the distribution $P(s)$

$$P(s) = r(s) \int_s^\infty P(x) \, dx \qquad (2)$$

The Poisson law follows if the level repulsion function $r(s)$ is unity no level repulsion whereas the Wigner's follows from the assumption of linear repulsion $r(s) \propto s$. It is known that in general the dynamics of a Hamiltonian is neither the Poisson type nor the Wigner's but both types of motion coexist. The Brody law describes the system which is an interpolation of the Poisson type and Wigner's [1-3].

2 Theory expansion of statistical properties in energy levels

However so far these theories are only limited to nondegenerate spectra having little concern with degenerate ones. As we all know when there are two levels with the same energy they are degenerate. Degeneracy comes from symmetry or accidental and appears generally in any energy level spectrum. A nondegenerate spectrum is only the special case when all the degeneracies tend to 1. Evidently the development of the statistical theory of fluctuation in degenerate spectra can not only further perfect the research of level statistics but also help us to penetrate the complex structure of various quantum systems. Therefore whether from the theoretical angle or under the consideration of the practical application to observed spectra this kind of extension and development is of great necessity. We have made some progress in the study of degenerate spectra recently [11]. The main idea is for a given degenerate spectrum

$$e_i \quad g_i \qquad\qquad i = 1, 2, \dots, n \qquad (3)$$

where e_i is energy of the ith level and g_i its degeneracy $\sum_{i=1}^n g_i = N$. Instead of the relationship between degeneracies and symmetries of the system we pay our attentions to how to analyze the data of the energy levels obtained from experimental measurements or numerical calculations. We know that levels in Eq. 3 are

correlated and the correlations come from three factors a relations among the degenerate levels b relations among the nondegenerate levels and c relations between degenerate and nondegenerate levels respectively. Obviously the neighbor spacings of degenerate levels are 0 and the level repulsions among them are also 0 so these degenerate levels consist of a sub-spectrum which can be thought of a random spectra

It is known that the random spectra are well studied now. The other two correlations b and c constitute another sub-spectra which is named after the regular spectrum of Eq. 3

$$e_i \quad g_i \qquad\qquad i = 1, 2, \dots, n \qquad (4)$$

For simplicity if only the correlations b are to be considered then the reduced nondegenerate spectrum of Eq. 3

$$e_i \qquad\qquad i = 1, 2, \dots, n \qquad (5)$$

is obtained. Therefore it can be dealt with in the theory framework of the nondegenerate spectra. Obviously there are some relations between Eq. 4 and 5. Let

$$N(e) = \sum_{i=1}^n \Theta(e - e_i) \qquad (6)$$

be the spectral staircase function which counts the number levels below e where $\Theta(x) = \begin{cases} 0 & x \leq 0 \\ 1 & x > 0 \end{cases}$ is the unit step function. The degenerate fluctuation spectrum

$$\varepsilon_i \quad g_i \qquad\qquad i = 1, 2, \dots, n \qquad (7)$$

can be obtained from Eq. 6 by means of weighted polynomial expansion fitting ε_i is the fluctuation from the average part. Usually the NNS distribution spectral rigidity fractal dimension FD function etc. are used to describe the statistical character of energy levels. The NNS distribution $P(s)$ is simply the probability for finding a level with separation s to its neighbor in Eq. 7. So it relates to the structure of the corresponding spectrum in detail. If the accumulative function $N(\varepsilon)$ of Eq. 7 is divided into M sub-stretches by the unit of length L then the spectral rigidity is the average of the least-square deviation of the accumulative function in each sub-stretch i. e.

$$\Delta_3(L) = \frac{1}{M}\sum_{i=1}^{M}\frac{1}{L}\left\{\underset{A_j,B_j}{\text{Min}}\sum_{n_j}\left[N(\varepsilon_j) - A_j\varepsilon_j - B_j\right]^2\right\}$$

(8)

where the coefficients A_j and B_j are determined through the linear fitting process, and $N(\varepsilon_j) = \sum_i (\varepsilon_j - \varepsilon_i)$. Unlike the NNS distribution, the spectral rigidity is concerned with the long-range interaction in the spectrum. Furthermore, the FD function for energy levels was introduced by Cederbaum *et al.* [7]. They firstly mapped the spectra into a set of n points in the interval [0, 1]. Each point was covered by a bar of length δ with $\delta/2$ on each side of the point. Once δ exceeds the smallest distance between two points, the bars overlap and the coarse-graining is done by the union of the overlapping bars of lengths l_i ($i = 1, 2, \ldots, m$), then the fractal dimensional function for energy levels is

$$D = \frac{\sum_{i=1}^{m}P_i\ln P_i}{\sum_{i=1}^{m}P_i\ln l_i}$$

(9)

where P_i is the probability that ε_j ($j = 1, 2, \ldots, N$) falls in the coarse-graining l_i, and can be calculated as $P_i = 1/n_i$, where n_i is the number of levels falled in l_i. The vibrational energy levels of H_2O, NH_3, CH_4 etc. are studied in this way, and some interesting results are obtained [11], all their regular spectra and reduced nondegenerate ones are no longer the Poisson type. Furthermore, the deviations to the Poisson law for the reduced nondegenerate spectrum are larger than those of their regular ones. With the increasing of degeneracy, these deviations decrease. Even a low Poisson law with a smaller FD function than that of Poisson type was obtained in the studying of an ideal model such as the quantum system that a particle moves in a three dimensional box (PMTDB) [13]. However, no molecule behaving like the low Poisson law has been reported yet.

It is well know that C_6H_6 is famous for its speciality in structure. Obviously, this speciality will be also reflected in the statistical behaviors of its vibrational energy levels. On the other hand, the special structure will be further exposed if its statistical properties are well studied. In this letter, we firstly review the statis-

tical character of the PMTDB system. Then some new types of statistical character are introduced. The statistical properties of C_6H_6 are to be analyzed in the new formalism.

For a PMTDB system with mass μ of the particle and the length (a_1, a_2, a_3) of the box [13], the Harmiltonian and the scaled energy are

$$H(I) = \frac{\pi^2}{2\mu}\left(\frac{I_1^2}{a_1^2} + \frac{I_2^2}{a_2^2} + \frac{I_3^2}{a_3^2}\right)$$

(10)

$$U(lm) = \frac{\pi}{3}\left(ABm_1^2 + \frac{B}{A^2}m_2^2 + \frac{A}{B^2}m_3^2\right)^{3/2}$$

(11)

where $A = \left(\frac{a_2}{a_1}\right)^{2/3}$, $B = \left(\frac{a_3}{a_1}\right)^{2/3}$. Its energy levels can be obtained through Eq. (10) and (11) if the parameters A and B are given, and the fluctuation spectrum is unfolded from the accumulative function $N(\varepsilon)$ by means of the polynomial expansion fitting. After a detailed investigation, it is found that, for the PMTDB system, both the maximum value of the NNS distribution and the spectral rigidity values are larger than that of the Poisson type, but the FD function is smaller than the Poisson type's [13]. It is different with the normal types such as the Brody law, of which the spectral rigidity is smaller than that of the Poisson but the FD function is larger than the Wigner's, so it is a completely new type which is called the low Poisson type due to the fact that the values of the FD function are smaller or lower than the Poisson law's.

It is time to expand or systemize the formalism for the possible laws of the statistical behaviors. The spectral rigidity and the FD function of the two universal types, i. e. the Poisson law and Wigner law, are shown in Fig. 1 and Fig. 2 respectively. The y-coordinates of Fig. 1 and Fig. 2 are the FD function D, spectral rigidity Δ_3 respectively, and the x-coordinates are the ratio $\delta/\bar{s}$ of the measured length δ to the average value $\bar{s}$ of the levels, the length of the measured unit L. From Fig. 1 and Fig. 2, it is easy to know that bounded by the two curves of Poisson law and Wigner law, there are three regions located between or beside them, the values fall in the intervals between them, i. e. the spectral rigidity is smaller than that of the Poisson type but larger than the Wigner, while its FD func-

tion is smaller than that of the Wigner but larger than the Poisson which has already been named as the Brody type. The other two unlabeled regions may be called the low Poisson law of which the spectral rigidity is larger than both the Wigner type and the Poisson type but the FD function is smaller than both that of the two types and the supper Wigner law which is just the opposite case compared with the low Poisson law. If the character is distinguished in more details maybe there are some spectra which can be called the nearly Poisson type or the nearly Wigner type which lies nearly along the Poisson curve or the Wigner curve.
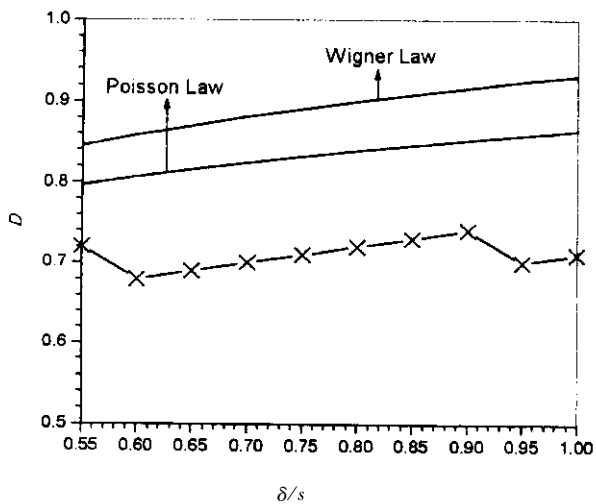

Fig. 1   The scope of fractal dimension function for
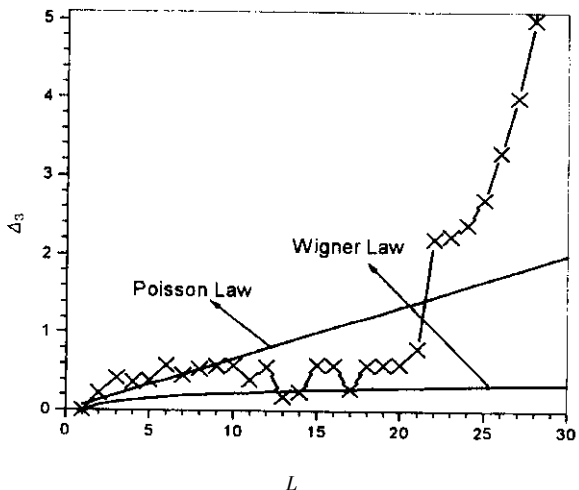different types of the statistical character

Fig. 2   The scope of spectral rigidity for different
types of the statistical character

3   Results

Now we are to analyze the statistical character of the vibrational energy levels in C_6H_6. The vibrational energy level spectrum of C_6H_6 has been calculated through the self-trapping quantum theory [14–17]

$$\left(i \frac{d}{dt} - \omega_0 \right)\bar{A} + M\bar{A} + \lambda \times$$

$$\text{diag}\left(|A_1|^2 \ |A_2|^2 \ \cdots \ |A_6|^2 \right)\bar{A} = 0 \qquad (12)$$

where $\bar{A} = \text{col}\left(A_1 \ \cdots \ A_6 \right)$ and the parameters needed for the calculation are the intension of the self-trapping interaction $\lambda = 114.61$ the resonant frequency $\omega_0 = 3159.13$ and the dispersion matrix

$$M = \begin{bmatrix} 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_2 & \varepsilon_1 \\ \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_2 \\ \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 \\ \varepsilon_3 & \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 \\ \varepsilon_2 & \varepsilon_3 & \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 \\ \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_2 & \varepsilon_1 & 0 \end{bmatrix} \qquad (13)$$

where $\varepsilon_1 = -4.91$ $\varepsilon_2 = -1.32$ $\varepsilon_3 = 1.61$. From the 3-th to 6-th exited state 896 levels are obtained through Eq. (12) and these levels consist of the spectrum to be studied. In the spectrum of C_6H_6 there are many levels with the intervals larger than 10^3 cm^{-1}. In practice we take two levels to be degenerate when their interval is smaller than 1 cm^{-1}. Doing in this way we find the average degeneracy is nearly 13.0. There will be unignored errors in the fluctuation spectrum if it is unfolded by means of the weighted polynomial expansion fitting. Fortunately in a way the speciality of the structure in C_6H_6 can be deduced from its reduced nondegenerate spectra Eq. (5) so we focus on the studying of Eq. (5).

For convenience we make use of the FD function and the spectral rigidity to demonstrate the statistical properties in C_6H_6. Its statistical characters have been analyzed and the results are also shown in Fig. 1 and Fig. 2. The curves consisting of" × " in both Fig. 1 and Fig. 2 are for the FD function and the spectra rigidity of the reduced nondegenerate levels of C_6H_6 respectively. From Fig. 1 we know that its FD function is smaller than both the Wigner law and the Poisson

law and maybe it is the low Poisson type. To confirm our guess we further analyze the character implied in the spectral rigidity. From Fig. 2 we know when L is small the character of the spectral rigidity Δ_3 is not clear because it fluctuates between the Poisson law and the Wigner law. However with increase of L the values of Δ_3 increase quickly and finally far above the Poisson curve. It is no doubt the spectral rigidity is the low Poisson type too. It is clear now that both the FD function and the spectral rigidity show the statistical character in the reduced nondegenerate spectrum of the vibrational levels of C_6H_6 is the low Poisson type. We note that the spectral rigidity of the reduced nondegenerate spectra is larger than that of regular one but the FD function the smaller. It is easy to get that if the statistical character of the reduced nondegenerate spectra is the low Poisson type the regular one must be the low Poisson type because the value of the FD function of the regular spectra will be smaller than the reduced one's but the spectral rigidity the larger. So we conclude that the statistical behaviors of C_6H_6 follow by the low Poisson law. In addition both the statistical character of the vibrational levels in C_6H_6 and the PMTDB system are the low Poisson type maybe this suggests that there are some relations in the dynamic behavior between them. This is another topic to be studied and we do not try to deal with it in details in this letter.

4　Conclusion

In summary we have studied the statistical properties of the reduced nondegenerate spectrum in the vibrational levels of C_6H_6. It is shown that the statistical character in C_6H_6 is the low Poisson type. This kind of the statistical character is the first time to be observed in the molecule system. It not only shows the speciality in the structure of C_6H_6 but also provides some new and interesting topics to be studied such as the similarity between the dynamic behavior in C_6H_6 molecule and the PMTDB system.

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